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On the determination of Sayre's constant for equal atom crystals

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Abstract : The estimation of Sayre's constant for equal atom structures, by using direct graphical and numerical method is described. The method is verified by selecting a set of structure factors, with known phases, which satisfied Sayre's equation The efficiency of the method are tested on equal atom structures The results show that the present procedure of estimation of Sayre's constant is quite satisfactory.

Keywords : Sayre's constant, atomic scattering factor

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Sayre's equation was originally developed for estimation of phases of the structure factors. This was carried out by considering a triplet of structure factors– F_h, F_k, F_{h-k} assuming that the constituent molecules contain equal and point atoms. If of these, the phases of two structure factors are known, Sayre's equation predicts the phase of the third structure factor with some probability. Hence for the light atom structures, it is useful to derive the value of the Sayre's constant, $\theta(s) = f(s)/g(s)$, where $f(s)$ is the scattering factor of the real atom and $g(s)$ is that of the squared atom. Again Main [1], Debaerdemaeker *et al* [2] described the methods of algebraically determining the phases of the structure factors in terms of Sayre's equation. However, Main (loc cit) has shown that the Sayre's constant depends upon the atomic shape and can not be exactly determined by the usual assumption of Gaussian distribution of electrons in the atom resulting in a Gaussian form factor. Therefore, it has been considered necessary to evaluate the constant $\theta(s)$ by using the direct graphical and numerical methods. Since the atomic numbers of light atoms mostly lie in the neighbourhood of these of carbon atom, the value of $\theta(s)$ has been worked out for carbon atom only, in the present case.

Sayre's equation [3] may be written as

$$F_h = \theta_h G_h, \tag{1}$$

where $G_h = V^{-1} \sum F_k F_{h-k}$ and $\theta_h = f_h / g_h$.

Here, f_h = atomic scattering factor of the atoms in the molecule (considered to be identical) and g_h = the atomic scattering factor of the corresponding squared atoms.

Assuming that the atoms have special electronic environment which gives rise to the atomic scattering factor, described by the Gaussian relation as,

$$f = Ze^{-ps^2}, \tag{2a}$$

where Z is the atomic number of the atom with the scattering factor f, p being the shape factor and s is the direction of the scattering as given by

$$S = (2 \sin \theta / \lambda). \tag{2b}$$

Here, θ is the half angle between the incident and the scattered beam and λ is the wave length of X-rays scattered by the atom. Eq (2a) is an approximation which may not be fully valid for many atoms. Again for the atoms obeying eq. (2a) and having the same shape factor p, the root mean square of structure factor is given by

$$\langle F^2 \rangle^{1/2} = \sqrt{\sum_j f_j^2} = \left(\sqrt{\sum_j Z_j^2} \right) e^{-ps^2},$$

(j varying from 1 to the total number of atoms in the unit cell), has a Gaussian distribution in s-space of reciprocal lattice space.

Since the electron density of a real atom is the Fourier transform of $f(s)$ and that of the squared atom is the Fourier transform of $g(s)$, those are respectively given by

$$\rho(r) = v^{-1} \int_0^s f(s) \cos 2\pi rs \, ds, \tag{3a}$$

$$\rho^2(r) = v^{-1} \int_0^s g(s) \cos 2\pi rs \, ds, \tag{3b}$$

where v = volume of the atom and r = radius of the atom. In case of a crystal, the normalised value of $\rho(r)$ is given by

$$\rho_N(r) = \rho(r) \Big/ \sqrt{\left(\sum_j Z_j^2 \right)}$$

and $g(s)$ is given by

$$g(s) = \int_0^R [\rho_N(r)]^2 \cos 2\pi rs \, dr. \tag{3c}$$

For the purpose of determining $\theta(s)$ from the known data regarding $f(s)$ against s [4] for carbon atom, the corresponding value of $\rho(r)$, $\rho^2(r)$ and $g(s)$ were evaluated from

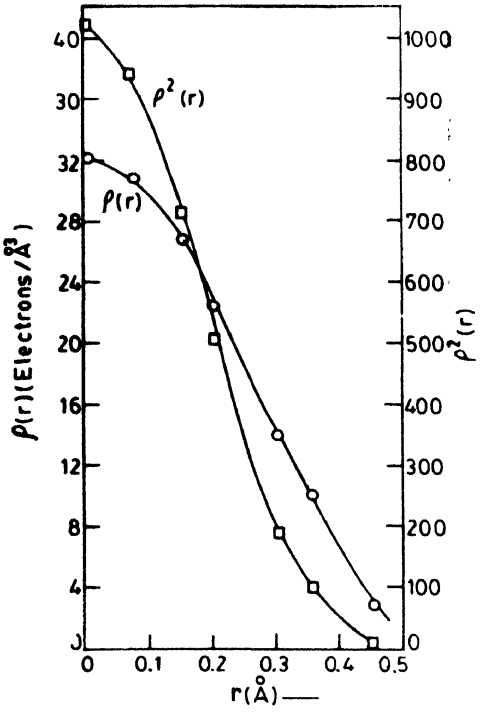

Figure 1(a). $\rho(r)$ and $\rho^2(r)$ against r.

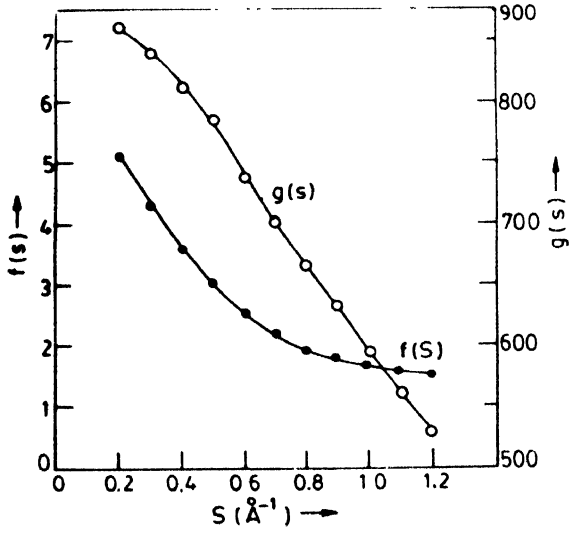

Figure 1(b). $f(s)$ and $g(s)$ against s.

eq. (3), neglecting the volume of the atom, for different values of r. The curves, drawn for $\rho(r)$, $\rho^2(r)$ against r and those for $f(s)$, $g(s)$ against s, are shown in Figure 1. From these

values of $f(s)$ and $g(s)$ the values of $\theta(s)$ have been obtained for different values of s. With this value of $\theta(s)$, the structure factor has been computed from eq. (1). The absolute values of F_h and $\theta_h G_h$ may be compared by means of zero check [5] which is given by

$$Z_0 = \sum\left(|F_h| - |\theta_h G_h|\right) / \sum |F_h \tag{4}$$

The calculations were carried out on the structures, the details of which are presented in Table 1. For this purpose, in case of each sample, a set of F_h-values has been

Table 1. The test samples

Crystal	Molecular formula	Formula units in the unit cell	Space group
(a) α-naphthil (α-NAP) [6]	$C_{22}H_{14}O_2$	2	$P\bar{1}$
(b) 2,6-dibutyryl 4-methyl phenol (TANS) [7]	$C_{15}H_{20}O_3$	2	$P\bar{1}$
(c) 5,9-dimethoxy-3, 3,8-trimethyl-7 10-dihydro-3H-naphthol [2, 1b] pyran-7,10-dion (CANON 2) [8]	$C_{18}H_{18}O_5$	4	$P2_1/n$
(d) 4-dydroxy mono-phenyl butazone (DHAN) [9]	$C_{13}H_{16}N_2O_3$	4	$P2_1/n$

Table 2. The values of F_{hkl} (experimental), θ_{hkl}, G_{hkl} and Z_0 for reflections from α-NAP.

hkl	F_{hkl}	$\theta_{hkl} G_{hkl}$	$\lvert F_{hkl} \rvert - \lvert \theta_{hkl} G_{hkl} \rvert$	Z_0
$1\bar{4}1$	32.5	34 68	−1.38	
$5\bar{1}2$	−24.3	−25.54	−1.24	
$3\bar{3}4$	19.7	20.47	−0 77	0.08
$\bar{8}\bar{6}2$	12.6	12.87	−0.27	
$10\bar{5}0$	−12.4	−13.28	−1.18	
$6\bar{3}5$	8.5	12.19	−3.69	

selected with known phases, which satisfy the Sayre's equation. From the findings of Mitra and Das [10], the signs of the structure factor of the interacting and the resulting reflections, of the test samples, have been accepted through Cauchy channel. Using these signs, the structure factor F_h, of a reflection h, has been determined from Sayre's relation [eq. (1)]

with the help of the calculated scale factor θ_h to match the magnitude of F_h and that of $\theta_h G_h$. Table 2 shows one such example (for the structure α-NAP) for six basic vectors. Similar calculations were carried out for other structures also.

Table 3 shows the derivation of the value of structure factor of one basic reflection for each of four crystals under study by the application of Sayre's relation (loc cit).

Table 3. Comparison of values of F_{hkl} and $\theta_{hkl} G_{hkl}$ for the test samples

Crystal	Space group	*hkl*	F_{hkl} (exp)	$\theta_{hkl} G_{hkl}$
α-NAP	$P\bar{1}$	$5\bar{1}2$	-24.3	-25.54
TANS	$P\bar{1}$	155	4.1	4.64
CANON 2	$P2_1/n$	$21\bar{1}0$	-15.3	-17.37
DHNV	$P2_1/n$	432	10.2	10.46

Table 4 shows the Z_0 values for each of the test structures.

Table 4. The values of the zero check for the test samples.

Crystal	Space group	Values of Z_0
α-NAP	$P\bar{1}$	0.08
TANS	$P\bar{1}$	0.09
CANON 2	$P2_1/n$	0.16
DHAN	$P2_1/n$	0.08

The results, presented above, show that the agreement within the Sayre's equation is quite satisfactory. This indicates that the method described for obtaining the scale factor θ_h in the case studied here, may be accepted for equal atom structure.

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